



**AFRL-SA-WP-TR-2016-0012**

# **Assessment of Metaborate Fusion for the Rapid Dissolution of Solid Samples: Suitability with the Northstar ARSIe**



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**July 2016**

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<b>REPORT DOCUMENTATION PAGE</b>				<i>Form Approved</i> <i>OMB No. 0704-0188</i>	
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<b>1. REPORT DATE (DD-MM-YYYY)</b> 19 Jul 2016		<b>2. REPORT TYPE</b> Technical Report		<b>3. DATES COVERED (From – To)</b> October 2011 – December 2012	
<b>4. TITLE AND SUBTITLE</b>  Assessment of Metaborate Fusion for the Rapid Dissolution of Solid Samples: Suitability with the Northstar ARSIIe				<b>5a. CONTRACT NUMBER</b> FA8650-11-C-6155	
				<b>5b. GRANT NUMBER</b>	
				<b>5c. PROGRAM ELEMENT NUMBER</b>	
<b>6. AUTHOR(S)</b> Annie Michaud, Dominic Larivière				<b>5d. PROJECT NUMBER</b>	
				<b>5e. TASK NUMBER</b>	
				<b>5f. WORK UNIT NUMBER</b>	
<b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b> Northstar Engineered Technology, LLC 706 Williamson St., Suite 2 Madison, WI 53703-4658				<b>8. PERFORMING ORGANIZATION REPORT NUMBER</b>	
<b>9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)</b> USAF School of Aerospace Medicine Aeromedical Research Department/FHO 2510 Fifth St., Bldg. 840 Wright-Patterson AFB, OH 45433-7913				<b>10. SPONSORING/MONITOR'S ACRONYM(S)</b>	
				<b>11. SPONSOR/MONITOR'S REPORT NUMBER(S)</b> AFRL-SA-WP-TR-2016-0012	
<b>12. DISTRIBUTION / AVAILABILITY STATEMENT</b>  DISTRIBUTION STATEMENT A. Approved for public release. Distribution is unlimited.					
<b>13. SUPPLEMENTARY NOTES</b> Cleared, 88PA, Case # 2016-4620, 19 Sep 2016.					
<b>14. ABSTRACT</b> The original goal of this project was to develop a rapid dissolution methodology for solid environmental samples and a crude pre-concentration of actinides (uranium, plutonium, thorium, americum) following the dissolution process to enable compatibility with the Automated Radionuclide Separation System-Environmental (ARSIIe) from Northstar Engineered Technologies. It was later required by the client during a subsequent meeting (August 2012, Québec City, Québec, Canada) that strontium be included in the list of analytes for which the sample preparation methodology should be applicable. This project was accomplished by executing a rigorous research and development strategy for soil dissolution that focuses on field deployment, efficiency, and the resulting dissolution being compatible with radiochemical separation performed by the ARSIIe using compatible designed protocols (necessary for controls and reproducibility). It was required by the client that the method of dissolution be simple (field-deployable), reliable, complete, and contained in as small a volume as possible (10- to 20-mL target). In addition, up to 1 gram of solid environmental samples needed to be solubilized through a lithium metaborate fusion technique, using the M4 Fluxer unit from Corporation Scientifique Claisse. Finally, the silicates naturally present in the environmental solid samples needed to be removed from the samples prior to actinide separation on the ARSIIe system. As a result of this project, two procedures were developed, one applicable to the pre-concentration of the actinides only and a second for the pre-concentration of both actinides and strontium. The main difference between the two procedures is during the pre-concentration step a different precipitating agent (titanium oxochloride and phosphoric acid) is used for the actinides and actinides/strontium pre-concentration, respectively.					
<b>15. SUBJECT TERMS</b> Actinides, soil, dissolution, radiochemical separation, strontium, lithium metaborate					
<b>16. SECURITY CLASSIFICATION OF:</b>			<b>17. LIMITATION OF ABSTRACT</b>  SAR	<b>18. NUMBER OF PAGES</b>  22	<b>19a. NAME OF RESPONSIBLE PERSON</b> William Bell
<b>a. REPORT</b> U	<b>b. ABSTRACT</b> U	<b>c. THIS PAGE</b> U			<b>19b. TELEPHONE NUMBER (include area code)</b>

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# TABLE OF CONTENTS

Section	Page
LIST OF FIGURES .....	ii
LIST OF TABLES .....	ii
1.0 SUMMARY .....	1
2.0 INTRODUCTION .....	1
3.0 RESULTS .....	3
3.1 Fusion .....	3
3.2 Silica Removal .....	4
3.2.1 Silicomolybdate Complex.....	4
3.2.2 Flocculation with PEG .....	6
3.3 Pre-Concentration.....	9
3.4 Conclusion.....	10
4.0 ACTINIDE SEPARATION ON THE ARSIIe SYSTEM – RESULTS .....	10
5.0 CONCLUSION.....	12
6.0 REFERENCES .....	12
APPENDIX – Protocols.....	14
LIST OF SYMBOLS, ABBREVIATIONS, AND ACRONYMS .....	16

## LIST OF FIGURES

	<b>Page</b>
Figure 1. M4 Fluxer from Corporation Scientifique Claisse .....	2
Figure 2. Synthesis of the insoluble silicomolybdate complex through the formation of soluble yellow $\text{H}_4\text{SiMo}_{12}\text{O}_4$ .....	5
Figure 3. Floc formation with polyethylene glycol and silica polymer .....	6
Figure 4. Procedure for silicate removal.....	8

## LIST OF TABLES

	<b>Page</b>
Table 1. Determination of Flux-to-Sample Ratio .....	3
Table 2. Parameter Variation and Recovery Yields for $\text{U}^{238}$ and $\text{Pu}^{242}$ .....	5
Table 3. Residual Silicates avec Flocculation in Glass Beaker or Polyethylene Cone .....	8
Table 4. Chosen Examples of Recovery Yield (Sr and Actinides) with Different Co-Precipitation Agent .....	9
Table 5. Tracer Recovery for Spiked Pure Nitric Acid and Soil-Borate Solutions.....	11

## 1.0 SUMMARY

The original goal of this project was to develop a rapid dissolution methodology for solid environmental samples and a crude pre-concentration of actinides (uranium, plutonium, thorium, americum) following the dissolution process to enable compatibility with the Automated Radionuclide Separation System-Environmental (ARSIIE) from Northstar Engineered Technology. It was later required by the client during a subsequent meeting (August 2012, Québec City, Québec, Canada) that strontium be included in the list of analytes for which the sample preparation methodology should be applicable.

This project was accomplished by executing a rigorous research and development strategy for soil dissolution that focuses on field deployment, efficiency, and the resulting dissolution being compatible with radiochemical separation performed by the ARSIIE using compatible designed protocols (necessary for controls and reproducibility).

It was required by the client that the method of dissolution be simple (field-deployable), reliable, complete, and contained in as small a volume as possible (10- to 20-mL target). In addition, up to 1 gram of solid environmental samples needed to be solubilized through a lithium metaborate fusion technique, using the M4 Fluxer unit from Corporation Scientifique Claisse. Finally, the silicates naturally present in the environmental solid samples needed to be removed from the samples prior to actinide separation on the ARSIIE system.

As a result of this project, two procedures were developed, one applicable to the pre-concentration of the actinides only and a second for the pre-concentration of both actinides and strontium. The main difference between the two procedures is during the pre-concentration step a different precipitating agent (titanium oxochloride and phosphoric acid) is used for the actinides and actinides/strontium pre-concentration, respectively.

## 2.0 INTRODUCTION

The acid-leaching technique is one of the most widely used for the determination of actinides in environmental matrices like soil and sediment [1,2]. However, while this technique allows the analysis of large sample sizes and produces solutions with low concentration of total salts, it is a time-consuming technique, often requiring numerous steps of digestion, evaporation, oxidation, and filtration [3]. It also requires the use of hazardous and concentrated acids like hydrofluoric acid and hot aqua regia if complete dissolution of soils samples is required. It has also been shown that this technique may not achieve a complete dissolution of refractory materials, like plutonium(IV) oxide [4]. Motabar et al. showed that up to 15-20% of residual uranium (U) and thorium (Th) remained in the undissolved zircon fractions after the treatment of a soil sample by acid digestion [5].

The fusion technique, which allows the complete solubilization of soil samples in a very limited number of steps, overcomes these problems. The fusion is performed by mixing the soil sample with a flux (often a lithium metaborate ( $\text{LiBO}_2$ ) or lithium tetraborate ( $\text{Li}_2\text{B}_2\text{O}_7$ ) salt, or a mixture of them) and by heating the mixture up to the melting point of the flux (around 1000°C with the borate flux). While initially fusion was performed in a muffle furnace in which the mixture of flux and samples was heated for several hours and then cooled down before being dissolved in warm acid, automated fusion units have been offered commercially for some time now. Figure 1 shows one example of this type of automated unit. In automated units, the sample and flux are mixed in a platinum crucible (95% platinum/5% gold) by the user and set on the

crucible support. The rest of the fusion process is then controlled remotely to apply a specific fusion procedure including heating the sample using propane burners and then pouring the sample into an aqueous solution. After just a few minutes, the components of the soil, including the silicate minerals, are completely dissolved into the molten flux through silicon-oxygen-borate interactions. When the right quantity of sample and flux is used, the fusion will give, in only a single step, a clear diluted acidic solution of actinides, alkaline earth metals, and other elements, which will be present as soluble nitrate (or chloride) complexes.



**Figure 1. M4 Fluxer from Corporation Scientifique Claisse.**

Although complete dissolution of the sample occurs, preliminary tests performed by Northstar on fused samples demonstrated that silica will interfere mechanically with the Automated Radionuclide Separation System-Environmental (ARSIIE) unit by clogging filters and cartridges. Therefore, the fusion protocol must be followed by a silicate removal step. As during the fusion, the silicate polymeric structures are decomposed into silicon (Si) monomer, making it is possible for the silicon monomer to interact with borate anions. However, when the melt is poured into an acidic media, soluble silicic acid monomers ( $\text{Si}(\text{OH})_4$ ) are formed. These molecules soon begin to condense to form polysilicic acids, and the condensation might continue until a silica gel is formed. Since the concentration of silicates in soil or sediment is high (up to 70-75% in silicon dioxide ( $\text{SiO}_2$ ) in some cases), the condensation products will mechanically reduce flow in the separation system and limit the use of the ARSIIE.

One common approach used for silicate removal is flocculation with polyethylene glycol (PEG). The high molecular weight polymer interacts with colloidal and subcolloidal silica in acidic aqueous solution (through hydrogen bonding) and leads to the formation of a precipitate, called a floc [6]. However, a survey of the literature showed that the complete or near complete removal of the silica with PEG takes several hours, usually more than 12-24 hours. Another strategy for silica removal is via the formation of a silicomolybdate precipitate. The latter approach is faster and requires less than 1 hour. Both procedures were tested and will be detailed in subsequent sections.

The volume requirement for the automated fusion (approximately 100 mL) and the addition of significant volumes of reagent required for the removal of silica will inevitably lead to solution with lower concentration of analytes. If such volumes were injected into the ARSIIE unit, more than 1 hour would be required to load a sample, an unacceptable time for a field-deployable methodology. To overcome this problem, pre-concentration of analyte via co-precipitation was proposed. Here, two approaches were investigated to determine a strategy suitable for actinides/alkaline earth elements.



### 3.0 RESULTS

#### 3.1 Fusion

To achieve complete dissolution of the sample, Corporation Scientifique Claisse (CSC) recommended a flux:sample ratio of 10:1. CSC also recommended using lithium metaborate, an alkaline flux, for the fusion of acidic samples such as solids containing a significant portion of SiO<sub>2</sub>. Conversely, lithium tetraborate, an acidic flux, will work well for the fusion of basic oxides (calcium oxide, for example). In complex matrices like environmental samples<sup>1</sup>, a blend of both borates could enable the complete dissolution of the sample. The ratio and the type of flux recommended by CSC are important parameters for the preparation of transparent and uniform disks for X-ray fluorescence analysis, the original instrumental application of the M4 unit. On the other hand, when the fusion is performed to prepare a solution (as in the case of this study), these parameters can be modulated to suit the need of a peculiar application.

To have complete dissolution of the soil and a clear acidic solution, several flux-to-sample ratios and flux blends were investigated (Table 1). The concentrations and the type of acid solution were also modulated. In some cases, dissolution was incomplete, but small undissolved particles of soil would eventually dissolve after heating the mixture at 95-100°C for approximately 30 minutes on a heating plate. Therefore, many sample-to-flux ratios, types of flux, or acid concentrations can be used.

**Table 1. Determination of Flux-to-Sample Ratio**

Quantity of Soil (g)	Quantity of Flux	Ratio of Flux	Acid	Acid Molarity (M)	State of Solution after Fusion	State of Solution after Heating Plate
0.3	3 g LiBO <sub>2</sub>	10	HNO <sub>3</sub>	6	Completely dissolved	NA
0.3	3 g LiBO <sub>2</sub>	10	HNO <sub>3</sub>	3	Completely dissolved	NA
0.5	2.25 g LiBO <sub>2</sub> , 0.75 g Li <sub>2</sub> B <sub>2</sub> O <sub>7</sub>	6	HNO <sub>3</sub>	6	Completely dissolved	NA
1.0	2.25 g LiBO <sub>2</sub> , 0.75 g Li <sub>2</sub> B <sub>2</sub> O <sub>7</sub>	3	HNO <sub>3</sub>	6	~90-95% dissolved	Completely dissolved
1.0	2.25 g LiBO <sub>2</sub> , 0.75 g Li <sub>2</sub> B <sub>2</sub> O <sub>7</sub>	3	HNO <sub>3</sub>	3	~90-95% dissolved	Completely dissolved
1.0	3 g LiBO <sub>2</sub>	3	HNO <sub>3</sub>	6	~90-95% dissolved	Completely dissolved
<b>1.0</b>	<b>3 g LiBO<sub>2</sub></b>	<b>3</b>	<b>HNO<sub>3</sub></b>	<b>3</b>	<b>~90-95% dissolved</b>	<b>Completely dissolved</b>
1.0	3 g LiBO <sub>2</sub>	3	HNO <sub>3</sub>	1.5	~90-95% dissolved	Completely dissolved
1.0	3 g LiBO <sub>2</sub>	3	HCl	2	~90-95% dissolved	Completely dissolved

Notes: Bold – proposed procedure. HCl = hydrochloric acid; HNO<sub>3</sub> = nitric acid; NA = not applicable.

The numerous tests performed showed that, for the type of soil evaluated, many sample-to-flux ratios, types of flux, or acid concentrations can be applied, as long as at least 3 grams of flux for a maximum of 1 gram of soil are used. For the final procedure, we suggest fusing 1 gram of soil with 3 grams of the lithium metaborate flux from CSC containing lithium bromide in 100 mL of 3M nitric acid solution (pouring step). The final fusion protocol is presented in the Appendix, as are the parameters used for the fusion on the M4 CSC unit.

<sup>1</sup> It is important to note that borate flux will only interact with oxides. Consequently, any environmental sample needs to be calcined and the metallic species must be in their oxidized form before the fusion.

## 3.2 Silica Removal

For the development of the procedure, two different types of environmental solids were used. One is a sediment sample collected from Ottawa River (collected near the Town of Chalk River, ON), whereas the other one is a soil sample from the vicinity of the Gentilly-2 nuclear power plant (Bécancour, QC). The content in silica of both samples was determined by inductively coupled plasma optical emission spectrometry (ICP-OES). The Ottawa River sediment and Gentilly-2 soil samples contained  $71.9 \pm 0.5\%$  and  $48 \pm 1\%$  of  $\text{SiO}_2$ , respectively.

**3.2.1 Silicomolybdate Complex.** Since the removal of the silica by flocculation with PEG was reported to be a long process in the literature, we decided, initially, to investigate the removal of silica through the rapid formation of an insoluble silicomolybdate complex. This strategy was based on a few documented experiments that demonstrated its applicability for the quantitative determination of silica in water [7-9]. After a few tests with pure  $\text{SiO}_2$  and with soil samples, it was found that the procedure used for the determination of silica in water could be extrapolated to digested solid sample analysis with minimal changes because of two important aspects:

1. The dissolved silica from fusion of soil samples is mostly under an  $\text{Si(OH)}_4$  form in diluted acid (HCl 2M in this case), which is the silica form that reacts the most rapidly with the ammonium molybdate tetrahydrate precursor (if dimers or trimers of the  $\text{Si(OH)}_4$  are present, they will also react with the molybdate compound, but the reaction is slower).
2. Aside from the phosphates, the other components of the soil matrix do not interfere with the reaction.

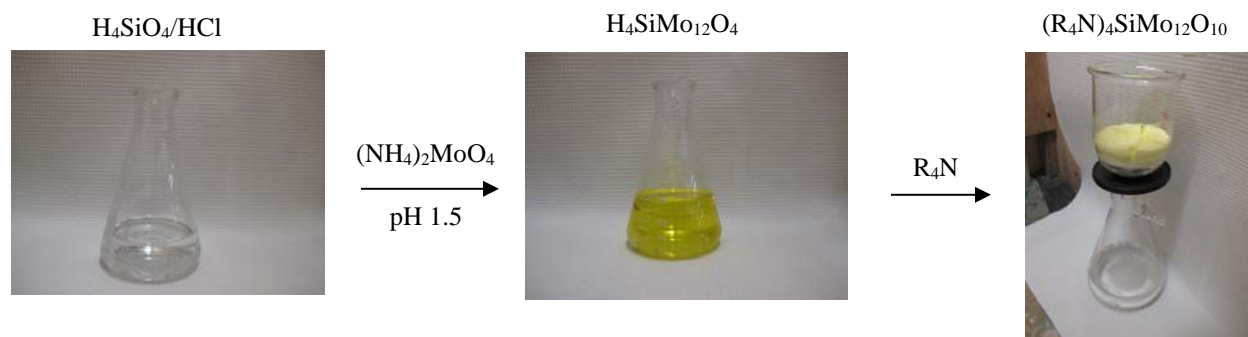
The removal of the silica through this approach is performed in three steps (Figure 2):

1. In HCl 2M,  $\text{Si(OH)}_4$  reacts rapidly with 15 equivalents of an ammonium molybdate precursor  $[(\text{NH}_4)_2\text{MoO}_4]$  to form, at pH 1.5, a soluble yellow silicomolybdate complex  $(\text{H}_4\text{SiMo}_{12}\text{O}_{40})$ .
2. In the presence of 6 equivalents of a quaternary amine or quinolone ( $\text{R}_4\text{N}$ , quaternary ammonium cation), the latter instantly precipitates as a light yellow ammonium silicomolybdate complex  $[(\text{R}_4\text{N})_6\text{SiMo}_{12}\text{O}_{40}]$ .
3. A rapid filtration on a 10- to 20- $\mu\text{m}$ -pore-size frit glass filter gives a clear, silica-free solution.

This silica removal process is very fast (the whole procedure with the fusion takes less than 1 hour) and is relatively simple to use. Experimental results showed that the residual silica, using the optimal procedure developed in this project, is less than 1% of the original content.

To be compatible with the objectives of the project, the fusion of several spiked samples of  $\text{SiO}_2$  or sediment for the recovery of  $\text{U}^{238}$  and plutonium ( $\text{Pu}^{242}$ ) was performed to determine if this process was also eliminating actinides from the solution. Different parameters, such as the number of equivalents of molybdate and amine, the pH, and time of reaction, were modulated (a few chosen examples are given in Table 2), and the recovery yield of U and Pu was determined with ICP mass spectrometry (MS) (unless specified otherwise). Unfortunately, even if the yields for the uranium recoveries were near quantitative, those for Pu were very low, near zero in some

cases. We believe that this observation is due to the fact that Pu(IV) is known to be complexed by amines, especially cationic quaternary amine, as it is shown by the high degree of retention of Pu(IV) on the commercial TEVA resins, where the functional groups are quaternary amines<sup>2</sup>.



**Figure 2. Synthesis of the insoluble silicomolybdate complex through the formation of soluble yellow  $H_4SiMo_{12}O_4$ .**  $H_4SiO_4$  = silicic acid.

**Table 2. Parameter Variation and Recovery Yields for  $U^{238}$  and  $Pu^{242}$**

Sample	MoO <sub>3</sub> Equiv	Amine	Amine Equiv	pH	Time of Reaction	% U or Pu	% Si Residual
SiO <sub>2</sub>	16	Quinoline	11	0	20 min	84 U	5
SiO <sub>2</sub>	15-28	Me <sub>4</sub> NCl	12	1.5	20 min	Final compound soluble (no precipitate)	
SiO <sub>2</sub>	15	Bu <sub>4</sub> NBr	12	0	20 min	92 U	2
SiO <sub>2</sub>	15	Bu <sub>4</sub> NBr	6	1.5	20 min	91 U	0
SiO <sub>2</sub>	15	Bu <sub>4</sub> NBr	6	1.5	24 h	100 U	14
Sediment	15	Bu <sub>4</sub> NBr	6	1.5	20 min	95 U	0
Sediment	15	Bu <sub>4</sub> NBr	6	1.5	20 min	24 Pu	---
Sediment	15	Bu <sub>4</sub> NBr	6	1.5	20 min	3 Pu	---

Note: Bu<sub>4</sub>NBr = tetrabutylammonium bromide; Me<sub>4</sub>NCl = tetramethylammonium chloride;  
MoO<sub>3</sub> = molybdenum trioxide.

To overcome this problem, it was proposed to oxidize Pu(IV) to Pu(VI) before the addition of the quaternary amine. Several attempts were made, using either sodium nitrate, potassium permanganate, cerium(IV), silver oxide, or potassium bromate as oxidizing agent and adding them at different moments in the procedure. We found that the best recovery yields were obtained with a mixture of the two following oxidants:

1. Sodium nitrate (77 mg), added directly in the platinum crucible so that oxidation begins during the fusion.
2. Silver oxide (56 mg), added in the Teflon beaker (containing the 2M HCl) solution so the VI oxidation state is maintained during the steps following the fusion.

<sup>2</sup> [http://www.eichrom.com/products/info/teva\\_resin.aspx](http://www.eichrom.com/products/info/teva_resin.aspx).

The highest recovery yield obtained using these conditions was 50% (determined by alpha analysis). However, since the use of oxidants increases the degree of complexity of the methodology developed and could modify the oxidation states of other actinides of interest in this project, we decided not to pursue this approach and to focus on the silica removal through PEG flocculation mainly by trying to minimize the flocculation time.

**3.2.2 Flocculation with PEG.** The use of high molecular weight polyethylene glycol polymer (with masses varying from 2000 to > 1,000,000) for the removal of silica is a well-known procedure, its use being first reported in 1965 for the reduction of silica content in aqueous media during hydrometallurgical processes [10,11]. Since then, many groups have used this technique for the silica removal of environmental or biological samples.

As mentioned earlier, the elimination of silicates by flocculation takes usually more than 12-24 hours. Through our extensive literature review, one exception was found. In the article from Croudace et al. [4], flocculation occurs rapidly (in 4 hours), but their experimental conditions were significantly different than those requested by the client: fusion was performed on 5 grams of soil sample and in an oven over 30 minutes. As the procedure described in this report was performed on 1 gram of dissolved soil sample obtained by automated fusion, the 4 hours flocculation time proposed by Croudace et al. was found ineffective, leading to a significant portion of silica still being dissolved in the supernatant due to the lower amount of Si dissolved.

Chemically the reaction between the silica and the PEG can be explained as follows. The oxygen of the ether group of the PEG polymer will interact with colloidal and subcolloidal silica in acidic aqueous solution through hydrogen bonding [12] ( $R_2O \cdots H-O-Si$ ); these interactions lead to the formation of a gelatinous precipitate, sometimes called a *floc* (Figure 3). It is important to note that the interaction of PEG with the silicic acid monomer will not form a precipitate; this is one of the reasons why the flocculation takes place over such a long period of time.

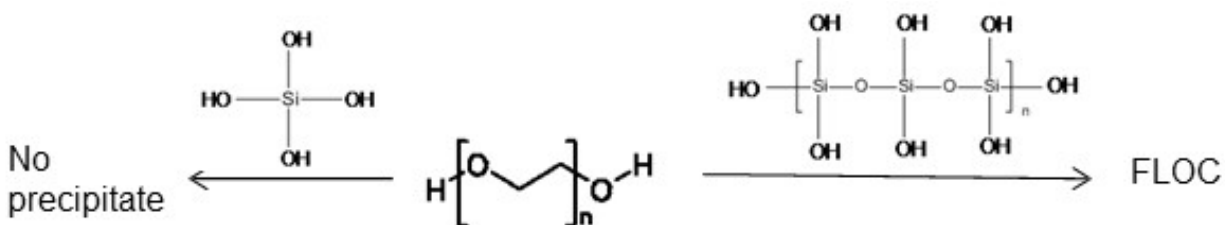


Figure 3. Floc formation with polyethylene glycol and silica polymer.

To reduce flocculation time, we attempted to accelerate the condensation reactions of the silicates. For this, several parameters of the general procedure described in the literature [4,13] (see Figure 4a) were modulated:

- Concentration of acid: Since condensation of silica is catalyzed by acid, we varied the nitric acid concentration (for the fusion step) from 1.5M to 6M.
- Dissolution time: We varied the dissolution time to see if an increase in the stirring

period promotes condensation before the addition of PEG. We tested different periods of time between 15 minutes and 3 hours, at  $T = 95\text{-}100^{\circ}\text{C}$ .

- Stirring time after PEG addition and evaporation time: These parameters were modulated for the same reason as the dissolution time. We determined the quality of the floc after different periods of time between 30 minutes and 6 hours.
- Final volume: With the idea that an increase in  $\text{Si}(\text{OH})_4$  concentration promotes condensation, the volume of the solution containing silicates was reduced from 100 mL to either 80, 70, 60, or 50 mL.
- Settling time: We verified if stirring had an impact on floc formation by stopping it immediately after PEG addition. For this, we concentrated the volume by evaporation before PEG addition.
- Centrifugation: We varied centrifugation time from 3 minutes to 10 minutes and the RPM from 3500 to 4500.

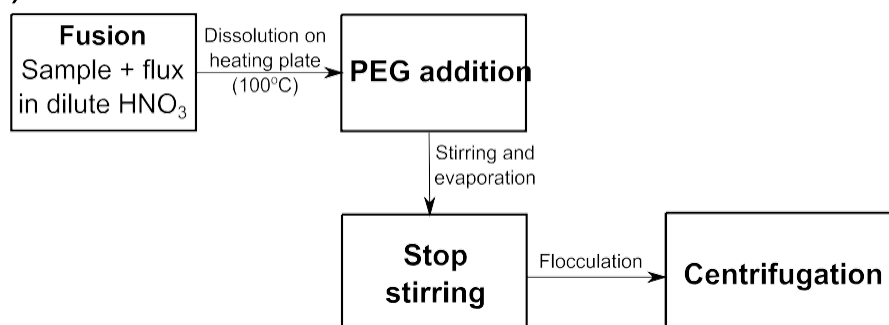
Figure 4 illustrates a typical procedure for the elimination of silica using PEG as reported in the literature. We optimized the procedure for the rapid removal of silica, as shown in Figure 4b. Experimentally, we determined that the best approach to determine if a significant portion of the silica was present in solution was by performing a simple final filtration on a  $0.2\text{-}\mu\text{m}$  filter. If the percentage of residual silicate in the supernatant is near zero, the filtration occurs without obstruction. If instead the content is high (example 10%), the filtration is difficult and will result in filters clogging.

After various attempts, it was determined that the most critical parameter for rapid flocculation was the stirring process. Stopping the stirring after PEG addition seems to lead to the formation of a better floc and the final filtration is performed without obstruction of the filter. It was also recognized that evaporation of the pouring solution from an initial volume of 100 mL to 70 mL prior to PEG addition would enhance the flocculation process.

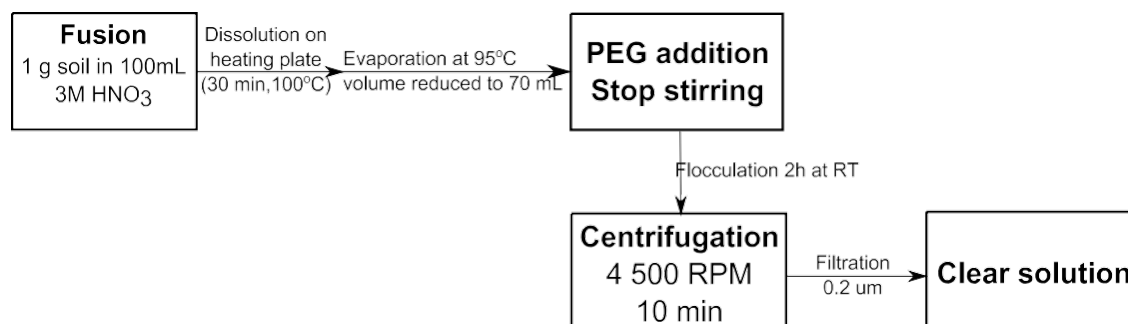
Originally, flocculation was done in a Pyrex beaker. To reduce the number of steps, we performed flocculation directly in the polyethylene cone to be used in the next step (centrifugation). For this to happen, we transferred the hot acid solution (reduced to  $\sim 70\text{ mL}$ ) in a 250-mL polyethylene cone and then slowly added PEG. Unfortunately, no floc was observed after 2 hours of flocculation and the  $0.2\text{-}\mu\text{m}$  filter clogged during filtration, meaning that a large quantity of silica was still in the supernatant.

As mentioned earlier, this is the consequence of a low degree of condensation of the silica, the chains being too short to form a floc with PEG. To initiate condensation and to compensate for the absence of condensation sites on wall of the glass beaker, we added 500 mg of silica gel in the cone before the addition of the solution containing the dissolved soil and the PEG. Initial tests with 70 mg of silica gel did not lead to any flocculation; therefore, the concentration of silica gel was increased to 500 mg, which seems sufficient. With these conditions we observed a usable floc after centrifugation. In addition, filtration on the  $0.2\text{-}\mu\text{m}$  filter was easily done. Table 3 shows the percentage of the residual silicates in the solution before the separation step on resins, depending on the soil and the vessel used for flocculation.

A)



B)



**Figure 4. Procedure for silicate removal. A) Initial general procedure. B) Final procedure proposed in this work.**

**Table 3. Residual Silicates with Flocculation in Glass Beaker or Polyethylene Cone**

Type of Soil	% of SiO <sub>2</sub> in Soil <sup>a</sup>	Flocculation in Beaker: Residual % SiO <sub>2</sub> <sup>b,c</sup>	Flocculation in Cone/Silica: Residual % SiO <sub>2</sub> <sup>b,c</sup>
Chalk River sediment	71.9±0.5		0.3±0.1
Chalk River sediment	71.9±0.5	0.30±0.04	
Gentilly 2	48±1		1.6±0.2
Gentilly 2	48±1	1.27±0.06	

<sup>a</sup>% SiO<sub>2</sub> in soil: mean and standard deviation determined on three measures (three fusions).

<sup>b</sup>Residual SiO<sub>2</sub>: mean and standard deviation determined on two measures (two fusions).

<sup>c</sup>Residual SiO<sub>2</sub> calculated on the estimated value of 100% of SiO<sub>2</sub>.

### 3.3 Pre-Concentration

As mentioned earlier, two final pre-concentration procedures were developed: one usable for actinides only and another for the pre-concentration of both actinides and strontium (Sr). The co-precipitation agent used for the pre-concentration of actinides is titanium oxychloride ( $\text{TiOCl}_2$ ), which is known to be insensitive to high content of alkaline earth metal [14] since the actinides co-precipitated at pH 7.<sup>3</sup> The co-precipitation procedure is rapid:  $\text{TiOCl}_2$  is added to the fresh, silica-free, acidic solution and the pH is increased to 7.5-8.0 with ammonium hydroxide ( $\text{NH}_4\text{OH}$ ). After centrifugation, the precipitate is dissolved in the smallest volume of acid and the resulting solution is ready for the actinide separation on resins after valence adjustment.

For the pre-concentration of both actinides and Sr, several co-precipitation agents were investigated, together with or in the absence of  $\text{TiOCl}_2$  (and added stepwise or in a one-pot reaction). The following co-precipitants—ammonium carbonate, ammonium oxalate, sulfuric acid, and phosphoric acid ( $\text{H}_3\text{PO}_4$ )—were investigated, and we also tested the addition of excess  $\text{Ca}^{2+}$  or  $\text{Ba}^{2+}$  to help the precipitation. For the actinide recovery, we spiked soil samples with  $\text{U}^{238}$ ,  $\text{Th}^{232}$ ,  $\text{Pu}^{242}$ , or  $\text{Am}^{241}$  (americium).  $\text{U}^{238}$  and  $\text{Th}^{232}$  were analyzed by ICP-OES, while  $\text{Pu}^{242}$  and  $\text{Am}^{241}$  were analyzed by alpha spectrometry (a few examples are given in Table 4). For the Sr analysis, we did not add any carrier. The amount of Sr was first determined in the Gentilly soil through the standard addition approach (725 ppm) and the recovery yield was assessed based on this value. However, the fraction of Sr in each phase (precipitate and supernatant) presented in Table 4 is calculated on the basis that 100% of Sr is recovered.

**Table 4. Chosen Examples of Recovery Yield (Sr and Actinides) with Different Co-Precipitation Agent**

Co-Precipitation Agent	Additional Ca or Ba Added?	Sr in Precipitation Agent Fraction (%)	Sr in Additional $\text{Ca}^{2+}$ (or $\text{Ba}^{2+}$ ) Fraction (%)	Sr in Supernatant ( $\text{NH}_4\text{OH}$ ) (%)	Actinide in Precipitation Agent Fraction (%)	Actinide in Supernatant ( $\text{NH}_4\text{OH}$ ) (%)
$\text{TiOCl}_2$	---	35-50	---	50-65	---	---
$(\text{NH}_4)_2\text{CO}_3$	$\text{Ca}^{2+}$	47	15	39	---	---
$(\text{NH}_4)_2\text{CO}_4$	$\text{Ca}^{2+}$	46	51	3	---	---
$\text{H}_2\text{SO}_4$	$\text{Ca}^{2+}$	73	2	25	---	---
$\text{TiOCl}_2$					$\text{U}^{238}$	$\text{U}^{238}$
$\text{TiOCl}_2 + \text{H}_3\text{PO}_4$	---	95±17		4.5±0.6	96±9 $\text{U}^{238}$	0.4±0.7 $\text{U}^{238}$
$\text{H}_3\text{PO}_4$	---	89±20		11±2	106±10 $\text{U}^{238}$	1±3 $\text{U}^{238}$
$\text{TiOCl}_2$					$\text{Th}^{232}$	$\text{Th}^{232}$
$\text{H}_3\text{PO}_4$	---	92±14		7.8±0.9	84±7 $\text{Th}^{232}$	2.1±0.1 $\text{Th}^{232}$
---					89 $\text{Pu}^{242}$	NA
$\text{TiOCl}_2$	---	37±5		62±6	58 $\text{Pu}^{242}$	NA
$\text{TiOCl}_2 + \text{H}_3\text{PO}_4$	---	---		---	64 $\text{Pu}^{242}$	NA
$\text{H}_3\text{PO}_4$	---	92±14		8±1	84 $\text{Pu}^{242}$	NA
$\text{H}_3\text{PO}_4$	---	93±13		7±1	100 $\text{Am}^{241}$	NA

Note: Standard deviation calculated on the cumulative error. Ca = calcium; Ba = barium.

<sup>3</sup> It was found, however, that up to 50% of Sr can precipitate at pH 7 in the presence of  $\text{TiOCl}_2$ .

Ammonium oxalate was one of the best co-precipitation agents for Sr, but would involve an additional step in the final procedure, since we would eventually have to ash the samples to get rid of this extremely strong ligand before separation on resin (used for the elution of many actinides with the ARSIIe unit). Acceptable recovery yields (for both Sr and actinides) were obtained with  $\text{H}_3\text{PO}_4$ . As for the procedure with this precipitant, it is exactly the same as the one with  $\text{TiOCl}_2$ , but the titanium compound is simply replaced with  $\text{H}_3\text{PO}_4$  (see the detailed protocol presented in the Appendix).

### 3.4 Conclusion

This silica removal process through the formation of an insoluble silicomolybdate complex was faster than the removal with PEG (1 hour versus approximately 4 hours). However, even if the recovery yields for uranium were quantitative, very low yields were observed for Pu(IV), due to its complexation with cationic quaternary amine.

To overcome this problem, the oxidation of Pu(IV) to Pu(VI) was performed in situ, and the highest recovery yield obtained was 50%. As the use of oxidants increasing the degree of complexity of the methodology developed, the removal of silica with PEG was subsequently chosen.

To reduce the general flocculation time (12 hours to several days), various tests were made to accelerate the condensation reactions of the silicates. It was realized that stopping the stirring during the flocculation step was the most critical parameter for rapid flocculation. With the optimized condition, flocculation occurs in 2 hours; the total removal procedure, including the fusion, takes less than 4 hours. To reduce the number of steps, flocculation can be performed directly in polyethylene cone (versus a beaker glass) provided that 500 mg of silica is first added to the cone.

Pre-concentration of actinides and Sr was easily performed with the addition of  $\text{H}_3\text{PO}_4$  as a pre-concentration agent. The co-precipitation procedure is rapid (the precipitate being instantaneously formed when the pH of the silica-free solution containing the actinides, Sr, and  $\text{H}_3\text{PO}_4$  is increased to 7.5-8.0 with  $\text{NH}_4\text{OH}$ ) and gives high recovery yield (>80-100% for Sr, Am, Pu, U, and Th).

The final sample preparation protocol is presented in the Appendix.

## 4.0 ACTINIDE SEPARATION ON THE ARSIIe SYSTEM – RESULTS

We started the separation tests on the ARSIIe system on November 16, 2012. 3M  $\text{HNO}_3$  solutions were first spiked (with  $\text{U}^{233}$ ,  $\text{Th}^{232}$ ,  $\text{Pu}^{242}$ ,  $\text{Am}^{241}$ , and Sr) and we gradually tested more complex solutions: borate or pre-concentration agent only in 3M  $\text{HNO}_3$  solution to complete borate-soil and pre-concentration agent solution (spiked with additional  $\text{Th}^{230}$  and  $\text{Am}^{243}$ ). For the development work, each set of resins was used six times, and a regeneration protocol using 0.1M ammonium bioxalate and 0.1M  $\text{HNO}_3$  solutions was applied between each separation (see Appendix). Valence adjustment was first performed using 100 to 200  $\mu\text{L}$  of sodium nitrite ( $\text{NaNO}_2$ ) 3M in water ( $\text{H}_2\text{O}$ ) and eventually 0.05M iron(II) [Fe(II)] sulfamate/ascorbic acid was used. This approach was believed to be effective, as it is commonly used in many separation protocols involving Pu performed using Eichrom products. However, based on a discussion with Northstar scientists, it was found that this approach would be detrimental to the project objective, as a proprietary resin was used in the ARSIIe unit. Modifications were done to the procedure



according to this new information. Details of the procedures are presented in the Appendix, and performances achieved by both valence adjustments are discussed below.

The recovery yields for HNO<sub>3</sub> spiked solutions were high, near quantitative for U<sup>233</sup> and Am<sup>241</sup>, and Sr total yield was between 88-100% [the recovery yield of Sr in the strontium fraction was generally around >75%, and the residual Sr was found in the barium or the recovery fraction (see Table 5)]. Very low yield for Pu<sup>242</sup> (5-15%) was observed when NaNO<sub>2</sub> was used for valence adjustment (even when additional volumes of HCl 0.1M/hydrofluoric acid 0.01M mixture were passed on the re-TRU resin to elute any residual Pu or when additional 3M NaNO<sub>2</sub>, using a total of 200 µL, was added). However, higher recovery yield for Pu, up to 82%, was observed when Fe(II) sulfamate/ascorbic acid was used for valence adjustment [15].<sup>4</sup>

**Table 5. Tracer Recovery for Spiked Pure Nitric Acid and Soil-Borate Solutions**

Fraction	Spiked 3M HNO <sub>3</sub> <sup>a</sup> (%)	Spiked 3M HNO <sub>3</sub> <sup>b</sup> (%)	Spiked Soil <sup>b</sup> (%)
Th	6±2 Th <sup>232</sup> <sup>c</sup>	103±19 Th <sup>232</sup> <sup>d</sup>	23±6 Th <sup>232</sup> <sup>d</sup>
U	105±11 U <sup>233</sup>	107±12 U <sup>233</sup>	89±9 U <sup>233</sup>
Am	100 Am <sup>241</sup>	96 Am <sup>241</sup>	85 Am <sup>241</sup> 85 Am <sup>243</sup>
Ba	(11±2 Sr)	(14±2 Sr)	(3.8 Sr)
Np			
Pu	91 Pu <sup>242</sup>	82 Pu <sup>242</sup>	86 Pu <sup>242</sup>
Sr	76±16 Sr	82±13 Sr	38.6 Sr
Recovery	(0.21±0.02 Sr)	(0.66±0.06 Sr)	(39.4 Sr)
Waste	(0.77±0.06 Sr)	(1.5±0.1 Sr)	(26.7 Sr)
Total Sr	88±18 Sr	98±16 Sr	108.5 Sr

Note: Natural strontium was added to tracer. Combined standard deviation calculated using the propagation of uncertainties approach. NP = neptunium.

<sup>a</sup>Valence adjustment: 100-200 µL NaNO<sub>2</sub> 3M/H<sub>2</sub>O.

<sup>b</sup>Valence adjustment: 0.05M Fe(II) sulfamate/ascorbic acid.

<sup>c</sup>100 µL of 1004 ppm solution used as a spike for ICP-OES analysis.

<sup>d</sup>400 µL of 989 ppb solution used as a spike for ICP-MS analysis.

Low yield for Th was observed (<10%) when 100 µg Th<sup>232</sup> was added as a spike (for ICP-OES analysis) to different solutions, from 3M HNO<sub>3</sub> solution to complete soil solution. However, adding a 250 times smaller quantity of Th<sup>232</sup> (0.4 µg) to 3M HNO<sub>3</sub> solution and performing the analysis on ICP-MS led to quantitative recovery yield when 3M HNO<sub>3</sub> solution was spiked. This observation would require further investigations to understand the underlying chemical reactions involved.

With the optimal conditions, final separations were performed on a solution resulting of the fusion of 500 mg of spiked soil and one with only 500 mg of soil. Recovery yields for U<sup>233</sup> and Sr were still high (89% and 108%, respectively), but lower yield was observed for Th (23% for Th<sup>230</sup>). The latter yield may be due to the formation of an insoluble Th-borate salt, which is known to occur after the fusion [16,17].

<sup>4</sup> Harvey JT. S3 results summary; 2012 Dec 11.

## 5.0 CONCLUSION

The goal of this project was to develop a rapid dissolution methodology for solid environmental samples and a crude pre-concentration of actinides (U, Pu, Th, Am) and strontium to enable compatibility with the ARSIIe from Northstar Engineered Technology.

The client required that up to 1 gram of solid environmental samples be solubilized through a lithium metaborate fusion technique. Numerous tests were performed in this study and showed that, depending of the type of soil, many sample-to-flux ratios, types of flux, or acid concentrations can be applied. However, for the final procedure, the fusion of 1 gram of soil with 3 grams of the lithium metaborate flux in 100 mL of 3M HNO<sub>3</sub> solution (pouring step) was suggested, with an additional heating of 20-30 minutes on a heating plate, this last step leading to a clear solution where the sample is completely dissolved.

The silicates naturally present in the environmental samples needed to be removed from the samples prior to actinide separation on the ARSIIe system. The removal through the formation of a silicomolybdate complex was faster than the removal with PEG, but led to very low yield for Pu(IV), due to its complexation with Bu<sub>4</sub>NBr, a reactive in the synthesis of the silicomolybdate compound. To avoid this interaction, the oxidation of Pu(IV) to Pu(VI) was performed, giving up to 50% yield for Pu. However the removal of silica with PEG was chosen since the use of oxidants increases the degree of complexity of the methodology.

The removal of the silicates with PEG occurs through a flocculation process, which is a long process, occurring generally over 12 hours to several days. To reduce this process, various tests were conducted, and it was realized that stopping the stirring during the flocculation step was the most critical parameter for rapid flocculation. With the optimized condition developed in this study, flocculation occurs in 2 hours; the total removal procedure, including the fusion, takes less than 4 hours. The flocculation step can be performed directly in a polyethylene cone in the presence of 500 mg of silica.

As a result of this project, two procedures were developed: one applicable to the pre-concentration of the actinides only and a second for the pre-concentration of both actinides and strontium. Pre-concentration of actinides was easily performed with TiOCl<sub>2</sub> as a pre-concentration agent, and H<sub>3</sub>PO<sub>4</sub> was used for the actinides and actinide/strontium pre-concentration. In both cases, the co-precipitation procedure is rapid and gives high recovery yield (>80-100% for Sr, Am, Pu, U, and Th).

The separation of the 3M HNO<sub>3</sub> solutions spiked with actinides on the ARSIIe gave high recovery results for all actinides and for Pu (>80% in each case) when Fe(II) sulfamate/ascorbic acid was used for valence adjustment.

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## APPENDIX

### Protocols

#### Procedure for the Digestion of Soil Sample – Fusion and Silicate Elimination:

1. In a platinum crucible, mix 500 mg of soil and 3 g of lithium metaborate (if the soil is spiked with any aqueous solution, leave the crucible in a stove at 100°C for 1-12 h for water evaporation).
2. Perform the fusion.<sup>5</sup> Drop the melt in a 150-mL Teflon beaker containing 100 mL 3M HNO<sub>3</sub> and a 38-mm stir bar.
3. Transfer the solution in a 150-mL Pyrex beaker; rinse the Teflon beaker with approximately 1.5 mL HNO<sub>3</sub> 3M (1x Pasteur pipet).
4. Cover with a watch glass; heat to low reflux for 30 min (dissolution step).
5. Remove the watch glass; evaporate under stirring until the volume is down to approximately 70 mL.
6. Transfer the hot solution in a 250-mL polyethylene cone containing 400-500 mg of silica gel.
7. Rinse the beaker with approximately 3 mL of 3M HNO<sub>3</sub> (2x Pasteur pipet).
8. While agitating mechanically with one hand, add  $\pm$  slowly (fast drop per drop) 1 mL of the PEG 6000 solution (10% in milliQ H<sub>2</sub>O).<sup>6</sup>
9. Let it rest for 2 h (flocculation step).
10. Centrifugation: 4500 rpm, 10 min, acceleration 9, deceleration 5.
11. Pour the supernatant in a 100-mL beaker. Add to the gel 15 mL HNO<sub>3</sub> 3M and shake it vigorously. You need to break the floc and disperse the aggregates in the acid solution.
12. Second centrifugation: 4500 rpm, 10 min, acceleration 9, deceleration 5.
13. Combine the supernatants in a beaker.
14. Filter the solution<sup>7</sup> on a 0.2- $\mu$ m filter (polyethersulfone) using a 30-mL syringe. Pour the filtrated solution directly into a 250-mL polyethylene cone.
15. Rinse the beaker with 2-3 mL HNO<sub>3</sub> 3M and filter again on the same filter.

#### Procedure for the Actinides Pre-Concentration:

1. Add 1 mL of TiOCl<sub>2</sub> 7%/HCl 4M solution.
2. Adjust the pH to  $\approx$  7.8-8.0 with NH<sub>4</sub>OH 28%.
3. Centrifugation: 3500 rpm, 5 min, acceleration 9, deceleration 5.
4. Discard the basic supernatant.
5. Rinse the precipitate with approximately 10 mL milliQ water and centrifuge again.
6. Dissolve the precipitate in 5 mL concentrate HNO<sub>3</sub>. Total volume  $\approx$  20-25 mL.
7. Add 500  $\mu$ L hydrogen peroxide 30% (hydrogen peroxide keeps the Ti in solution during the separation): solution turns red.

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<sup>5</sup> See Parameters section for the fusion.

<sup>6</sup> 5 g of polyethylene glycol formula weight (FW) = 6,000 dissolved in 50 mL milliQ water.

<sup>7</sup> Depending on the type of soil, the solution can be almost clear or contain visible silica (pieces or gel).

### Procedure for the Actinides and Strontium Pre-Concentration:

1. Add 500  $\mu\text{L}$   $\text{H}_3\text{PO}_4$  85%.
2. Adjust the pH to  $\approx 7.8$ -8.0 with  $\text{NH}_4\text{OH}$  28%.
3. Centrifugation: 3500 rpm, 5 min, acceleration 9, deceleration 5.
4. Discard the basic supernatant.
5. Rinse the precipitate with approximately 10 mL milliQ water and centrifuge again.
6. Dissolve the precipitate in 5 mL 8M  $\text{HNO}_3$ .
7. Adjust the pH to approximately pH 3 with  $\text{NH}_4\text{OH}$  28%.
8. Total volume should be around 15 mL.

### Procedure for the Valence Adjustment before ARSIIe Separation:

1. Transfer the solution in a 50-mL cone; rinse the 250-mL cone with 2-3 mL 3M  $\text{HNO}_3$ .
2. Add 0.3522 g L-ascorbic acid (FW 176.12, CAS 50-81-7).
3. Add 0.1942 g sulfamic acid (FW 97.09, CAS 5329-14-6).
4. Shake until total dissolution.
5. Add 3M  $\text{HNO}_3$  until total volume is 20 mL.<sup>8</sup>
6. Add 0.2780 g  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (FW 278.01, CAS 7782-63-0).
7. Shake until total dissolution.

Note: this valence adjustment step is performed the same day as the separation on ARSIIe.

### Parameters for the Fusion of 1 g of Soil (in Platinum Crucibles) on the M4 Fluxer

Parameter	F0 Heat	F1 Heat	F2 Heat	F3 Heat	F4 Heat	F5 Pour	F6 Cool
Gas	2	2	25	45	55	25	0
Crucible Speed	0	10	30	40	60	15	0
Time	00:05	00:30	00:30	01:00	03:00	00:10	10:00
Arm Position	0	0	20	30	40	55	0
Mold Arm Position	0	0	0	0	0	95	20
Arm Speed	99	99	99	99	99	99	99
Fan Speed	0	0	0	0	0	0	10
Magnetic Stirring Speed	0	0	0	0	0	90	99
Non-Wetting Agent	Off	Off	Off	Off	Off	Off	Off
Buzzer	On	On	On	On	On	On	On
Air Injector	Off	Off	Off	Off	Off	Off	Off

<sup>8</sup> The total concentrations should be 0.05M for Fe and 0.1M for each acid. See Grate et al. [15].

## LIST OF SYMBOLS, ABBREVIATIONS, AND ACRONYMS

<b>Am</b>	americum
<b>ARSIle</b>	Automated Radionuclide Separation System-Environmental
<b>Ba</b>	barium
<b>Ca</b>	calcium
<b>CSC</b>	Corporation Scientifique Claisse
<b>Fe</b>	iron
<b>H<sub>2</sub>O</b>	water
<b>H<sub>3</sub>PO<sub>4</sub></b>	phosphoric acid
<b>HCl</b>	hydrochloric acid
<b>HNO<sub>3</sub></b>	nitric acid
<b>ICP</b>	inductively coupled plasma
<b>LiBO<sub>2</sub></b>	lithium metaborate
<b>Li<sub>2</sub>B<sub>2</sub>O<sub>7</sub></b>	lithium tetraborate
<b>MS</b>	mass spectrometry
<b>NA</b>	not applicable
<b>NaNO<sub>2</sub></b>	sodium nitrite
<b>NH<sub>4</sub>OH</b>	ammonium hydroxide
<b>OES</b>	optical emission spectrometry
<b>PEG</b>	polyethylene glycol
<b>Pu</b>	plutonium
<b>Si</b>	silicon
<b>SiO<sub>2</sub></b>	silicon dioxide
<b>Si(OH)<sub>4</sub></b>	silicic acid
<b>Th</b>	thorium
<b>TiOCl<sub>2</sub></b>	titanium oxychloride
<b>U</b>	uranium